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**Polymer stabilised chiral nematic LC material light modulating cell -  
switchable between clear and light scattering modes by changing electric  
field and having stable intermediate colour reflecting states**

Patent Assignee: UNIV KENT STATE (UYKE-N)

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Patent Family:

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US 5384067	A	19950124	US 91694840	A	19910502	199510
			US 92885154	A	19920518	
EP 641372	A1	19950308	EP 92925047	A	19921030	199514
			WO 92US9367	A	19921030	
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			US 92885154	A	19920518	
			US 92969093	A	19921030	
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			US 92885154	A	19920518	
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DE 69229003	E	19990527	DE 629003	A	19921030	199927
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EP 742915      B1 E      G02F-001/137 Based on patent WO 9410260  
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Abstract (Basic): WO 9323496 A

Light modulating cell comprises light modulating material of liq. crystal (16) and polymer (15). The liq. crystal is a chiral nematic liq. crystal having positive dielectric anisotropy and including chiral material in an amt. effective to form focal conic and twisted planar textures (30). The polymer is distributed in phase separated domains (15) in an amt. that stabilises the focal conic and twisted planar textures in the absence of a field and permits the liq. crystal to change textures when a field is applied.

The cell is switched between a stable, colour reflecting stage that reflects a max. reference intensity and a stable light scattering state exhibiting min. reference intensity of reflection by applying a voltage pulse. By applying voltage pulses of varying magnitude, a continuum of stable states having colour reflectivity of an intensity between the max. and min. are obtd.

USE/ADVANTAGE - Light modulating cell is esp. a bistable light shutter which can be switched between a stable, optically clear state and a stable light scattering state by applying or removing an electric field. Material can operate in a light scattering mode in a field-OFF condition and clear in a field-ON condition or vice versa. The material exhibits minimal haze at all viewing angles in the clear state without any need for light-reducing polarisers. It does not require an active matrix to make a high-definition panel screen.

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Title Terms: POLYMER; STABILISED; CHIRAL; NEMATIC; LC; MATERIAL; LIGHT; MODULATE; CELL; SWITCH; CLEAR; LIGHT; SCATTERING; MODE; CHANGE; ELECTRIC; FIELD; STABILISED; INTERMEDIATE; COLOUR; REFLECT; STATE

Derwent Class: A85; L03; P81; U14; V07

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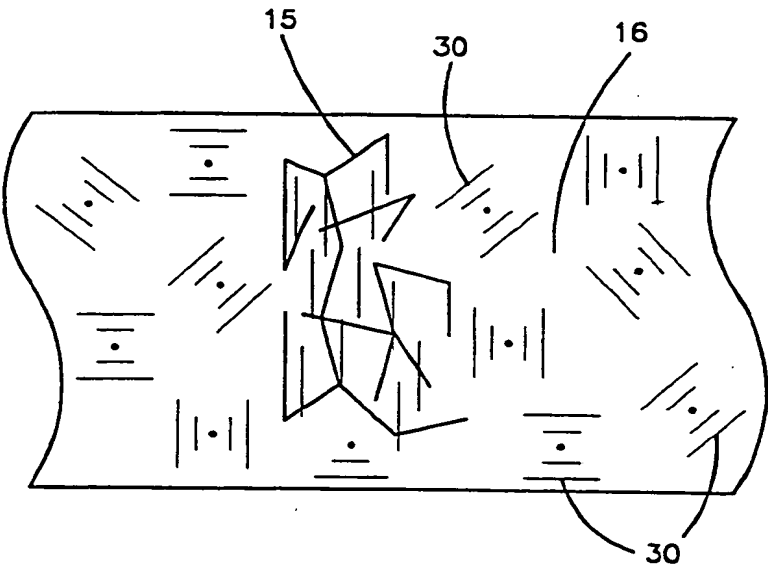
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<b>(21) International Application Number:</b> PCT/US92/09367 <b>(22) International Filing Date:</b> 30 October 1992 (30.10.92)  <b>(30) Priority data:</b> 07/885,154                   18 May 1992 (18.05.92)           US 969,093                   30 October 1992 (30.10.92)       US  <b>(71) Applicant:</b> KENT STATE UNIVERSITY [US/US]; East Main & Lincoln Street, Kent, OH 44242 (US).  <b>(72) Inventors:</b> DOANE, William, J. ; 1618 South Lincoln Street, Kent, OH 44240 (US). YANG, Deng-ke ; 826 Allerton Street, Kent, OH 44240 (US). CHIEN, Liang-Chy ; 4510 Forest Hill Road, Stow, OH 44224 (US).		<b>(74) Agent:</b> HEINKE, Lowell, L.; Watts, Hoffmann, Fisher & Heinke Co., 100 Erieview Plaza, Suite 2850, Cleveland, OH 44114-2214 (US).  <b>(81) Designated States:</b> CA, JP, KR, NO, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LIQUID CRYSTALLINE LIGHT MODULATING DEVICE & MATERIAL  <div style="text-align: center;">  </div>		
<b>(57) Abstract</b>  <p>A new liquid crystalline light modulating cell and material are characterized by liquid crystalline light modulating material of liquid crystal and polymer, the liquid crystal being a chiral nematic liquid crystal (16) having positive dielectric anisotropy and including chiral material in an amount effective to form focal conic and twisted planar textures, the polymer being distributed in phase separated domains (15) in the liquid crystal cell in an amount that stabilizes the focal conic and twisted planar textures in the absence of a field and permits the liquid crystal to change textures upon the application of a field. In one embodiment, the material is light scattering in a field-OFF condition and optically clear in a field-ON condition, while in another embodiment, the material is optically clear in a field-OFF condition and light scattering in a field-ON condition. In still another embodiment, the material exhibits stability at zero field in a colored, light reflecting state, a light scattering state and multiple stable reflecting state therebetween, as well as being optically clear in the presence of a field.</p>		

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## LIQUID CRYSTALLINE LIGHT MODULATING DEVICE & MATERIAL

This application was made in part with Government support under  
5 cooperative agreement number DMR 89-20147 awarded by the National Science  
Foundation. The Government has certain rights in this invention.

### BACKGROUND OF THE INVENTION

#### 10 Related Applications

This application is a continuation in part of U.S. Serial No. 07/694,840  
filed May 2, 1991, incorporated herein by reference, and U.S. Serial No.  
07/885,154, filed May 18, 1992, incorporated herein by reference.

#### 15 TECHNICAL FIELD

The present invention relates generally to liquid crystalline light  
modulating devices, and more specifically to new phase-separated polymeric-  
liquid crystalline display cells and materials which exhibit different optical states  
under different electrical field conditions and are characterized by a unique  
20 combination of properties, including optical multistability and haze-free light  
transmission at all viewing angles in either a field-ON or field-OFF mode.

### DESCRIPTION OF THE RELATED ART

Electrically switchable liquid crystal-polymer films intended for use in  
various electro-optical devices have been prepared by mechanical entrapment  
procedures. One such technique involves imbibing liquid crystal into micropores  
of a plastic or glass sheet. Another technique involves evaporation of water  
from an aqueous emulsion of nematic liquid crystal in a solution of water-soluble  
polymer such as polyvinyl alcohol or in a latex emulsion.

A different procedure offering significant advantages over mechanical  
entrapment techniques and the emulsification procedure involves phase  
separation of nematic liquid crystal from a homogeneous solution with a suitable  
synthetic resin to form a liquid crystal phase dispersed with a polymer phase.  
The resulting materials are referred to as polymer dispersed liquid crystal

(PDLC) films. Some of the advantages of PDLC films are discussed in U.S. Patent Nos. 4,671,618; 4,673,255; 4,685,771; and 4,788,900; the disclosures of which are incorporated by reference. PDLC films have been shown to be useful in many applications ranging from large area displays and switchable coatings for windows to projection displays and high-definition television.

The methods of phase separation can be carried out by polymerization initiated by addition of a curing agent, by ultraviolet light or by cooling into the region of immiscibility. Another method is evaporating a solvent from a matrix-producing composition of a solution of polymer and liquid crystal in the solvent.

In windows or displays as described above in which the ordinary index of refraction of the liquid crystal is matched to the refractive index of the polymer, the device appears most transparent (field-ON state) when viewed along the direction of the field which is usually normal to the viewing surface. Transparency decreases giving rise to increasing "haze" at increasing oblique viewing angles until an essentially opaque appearance is detected at an oblique enough angle. This condition of haze results from the fact that the farther the viewing angle is from the orthogonal, the greater is the perceived mismatch between the effective index of refraction of the liquid crystal and the refractive index of the matrix.

A further development of PDLC films disclosed in U.S. Patent Application Ser. No. 07/324,051, now U.S. Patent No. 4,994,204 issued February 19, 1991, involves the use of a birefringent polymer, e.g., a liquid crystal polymer. The PDLC film prepared with the birefringent polymer has the characteristic of displaying haze-free transparency for all directions of incident light. This is accomplished by matching the ordinary and extraordinary indices of refraction of the polymer to the ordinary and extraordinary indices of refraction of the liquid crystal.

PDLC films made with birefringent polymer can operate in the normal manner so that they are clear in a field-ON state and light scattering in a field-OFF state. Alternatively, the films can be made to operate in a reverse or "fail-safe" mode such that the material is clear in the absence of a field and is light scattering in the field-ON state.



DISCLOSURE OF THE INVENTION

The invention is an electrically switchable material which exhibits a unique combination of properties that afford significant advantages over preceding technology. For example, the new material can operate either in the mode of  
5 being light scattering in a field-OFF condition and clear in a field-ON condition or in the reverse mode of being clear in the field-OFF condition and light scattering in the field-ON condition. In both instances, the material exhibits minimal haze at all viewing angles when in the clear state.

Another important feature of the invention is that the material can be  
10 prepared so that it exhibits multiple optically different states, all of which are stable in the absence of an applied field. When incorporated in a display device, the material can be driven from one state to another by an electric field. Depending upon the magnitude and shape of the electric field pulse, the optical state of the material can be changed to a new stable state which reflects any  
15 desired intensity of colored light along a continuum of such states, thus providing a stable "grey scale." A low electric field pulse results in a light scattering state which is white in appearance. The application of a sufficiently high electric field pulse, i.e., an electric field high enough to homeotropically align the liquid crystal directors, drives the material to a light reflecting state that can be any desired  
20 color. The light scattering and light reflecting states remain stable at zero field. If a sufficiently high electric field is maintained, the material is transparent until the field is removed. When the field is turned off quickly, the material reforms to the light reflecting state and, when the field is turned off slowly, the material reforms to the light scattering state. Electric field pulses of various magnitudes  
25 below that necessary to drive the material from the stable reflecting state to the stable scattering state will drive the material to intermediate states that are themselves stable. These multiple stable states indefinitely reflect colored light of an intensity between that reflected by the reflecting and scattering states. Thus, depending upon the magnitude of the electric field pulse the material  
30 exhibits stable grey scale reflectivity. Application of mechanical stress to the material can also be used to drive the material from the light scattering to the light reflecting state.

A major advantage of the multistable material is that it does not require an active matrix to make a high-definition flat panel screen. The screen can be prepared without active elements at each pixel site and a multiplexing scheme used to address the display. This greatly simplifies production, increases yield  
5 and reduces the cost of the display.

Multiplexed flat panel liquid crystal displays are not new and have been developed primarily with super twisted nematic materials for applications such as lap-top computer screens where speed, contrast or color is not an important issue. Ferroelectric liquid crystals, which exhibit a surface stabilized bistable  
10 state, also can be multiplexed. These displays have been difficult to commercialize because the surface stabilization is not maintained under severe operating conditions. The material of the present invention provides several advantages in that the light scattering and light reflecting states are materially stabilized without requiring delicate surface conditions of the substrate. Display  
15 devices made with the material of the invention do not require polarizers which limit the brightness of the displays. Furthermore, color is introduced by the material itself without the need of color filters which also can reduce brightness.

The advantageous properties described above are achieved in the invention by providing a light modulating cell comprising a liquid crystalline light  
20 modulating material of liquid crystal and polymer, the liquid crystal being a chiral nematic liquid crystal having positive dielectric anisotropy and including chiral material in an amount effective to form focal conic and twisted planar textures, the polymer being distributed in phase separated domains in the cell in an amount that stabilizes the focal conic and twisted planar textures in the absence  
25 of a field and permits the liquid crystal to change textures upon the application of a field.

The addressing means can be of any type known in the art, such as an active matrix, a multiplexing circuit, electrodes, etc. The liquid crystal molecules in the vicinity of the polymer domains are anchored by the polymer. As a result,  
30 the new material can be made to exhibit different optical states, i.e., light transmitting, light scattering, light reflecting and stable grey scale in between these states, under different field conditions.

The material used to form the polymer networks is soluble with the chiral nematic liquid crystal and phase separates upon polymerization to form phase separated polymer domains. Suitable polymer materials may be selected from U.V. curable, thermoplastic and thermosetting polymers, including polymers  
5 formed from monomers having at least two polymerizable double bonds so as to be cross-linkable, polymethylmethacrylates, bisacrylates, hydroxyfunctionalized polymethacrylates and epoxy systems to name a few. The amount of polymer to be used depends upon the polymer. Useful results have been obtained with polymer contents ranging from about 1.5 to about 40% depending upon the  
10 polymer.

The chiral nematic liquid crystal is a mixture of nematic liquid crystal having positive dielectric anisotropy and chiral material in an amount sufficient to produce a desired pitch length. Suitable nematic liquid crystals and chiral materials are commercially available and would be known to those of ordinary  
15 skill in the art in view of this disclosure. The amount of nematic liquid crystal and chiral material will vary depending upon the particular liquid crystal and chiral material used, as well as the desired mode of operation. For normal and reverse mode cells, useful results can be obtained using from 0.5 to about 17% by weight chiral material based on the combined weight of nematic liquid crystal  
20 and chiral material and depending upon the chiral material used. A preferred range of chiral material is from about 1 to about 16%. For multistable cells, useful results have been obtained using from about 18 to about 66% by weight chiral material based on the combined weight of chiral material and nematic liquid crystal.

25 The wavelength of the light that is reflected by the material is given by the relation  $\lambda = np$ , where  $n$  is the average refractive index and  $p$  is the pitch length. Wavelengths above 800 nm are in the infra-red and those below 380 nm are in the ultra violet. In cells which operate in either the normal mode of being light scattering in a field-OFF condition and light transmitting in a field-ON  
30 condition or the reverse mode of being light transmitting in the field-OFF condition and light scattering in a field-ON condition, the chiral nematic liquid crystal has a pitch length effective to reflect light outside the visible spectrum, preferably in the infra-red spectrum. A preferred pitch length for normal mode

and reverse mode cells ranges from about 1.0 to about 4.0 microns. Liquid crystalline light modulating materials that operate in the normal and reverse modes have been prepared with chiral nematic liquid crystal containing from about 1 to about 16% by weight, chiral material based on the combined weight of nematic liquid crystal and chiral material. It will be understood that, in both instances, the weight amounts can vary depending upon the particular liquid crystal, chiral material and polymer used.

In carrying out the invention, the solution of liquid crystal and polymer (or polymer precursor) is introduced into a cell. Polymerization is initiated in any suitable manner, as by UV radiation, thermally etc., depending upon the polymer used. Under polymerization conditions, the polymer phase separates from the chiral nematic liquid crystal and forms phase separated polymer domains of polymer molecules.

While not necessary to the invention, in some instances it is preferable to treat the cell walls to provide for surface alignment of the liquid crystal molecules parallel to the cell walls, e.g., by providing the cell walls with rubbed polyimide layers or treating them with detergent or chemicals. This has the effect of improving transmission and response time in some reverse mode cells in the field-OFF condition.

In the case of normal mode cells, polymerization takes place in the presence of an electric field that aligns the liquid crystal molecules orthogonally to the cell walls. When polymerization has been completed and the electric field removed, the liquid crystal molecules in the vicinity of the polymer domains are anchored in a preferential homeotropic alignment. The surrounding chiral liquid crystal has a focal conic texture which results from competition between the forces in the cell, such as any surface effects of the cell walls, the electric field and the constraining effect of the polymer domains. In the field-OFF condition, the polymer-liquid crystalline material is strongly light scattering and the cell is opaque. In the field-ON condition, the focal conic texture reforms to homeotropic alignment so that the cell is optically clear. There is negligible variation or fluctuation of refractive index throughout the liquid crystalline material because of the homeotropic alignment of the liquid crystal molecules and the typically small amount of polymer in the composition. Therefore, the

cell is haze-free at all viewing angles. However, it should be noted that increasing the amount of polymer can have the effect of increasing the amount of haze.

In the case of reverse mode cells, polymerization takes place in the absence of a field. The liquid crystal molecules throughout the cell prefer a twisted planar structure. In the absence of a field, the cell is optically clear, since there is no reflecting or scattering in the visible light region. In a field-ON condition, the liquid crystal molecules have a focal conic texture in the presence of the field as a result of competition of the various forces in the cell, such as any surface effects, the electric field and the constraint of the polymer domains. In this condition, the cell is light scattering. For liquid crystal materials having suitably long pitch lengths, the material will return to the planar texture upon removal of the field.

The multistable color display cells are prepared by polymerizing and phase separating the liquid crystal-polymer solution either in zero field or in a field effective to align the liquid crystal directors. In both instances, the polymer domains that are created in the material serve to stabilize the light scattering state resulting from application of a low electric field pulse and the light reflecting state resulting from application of a high electric field pulse.

In the field-OFF condition with the liquid crystal molecules in a twisted planar texture parallel to the cell walls, the cell is in a colored light reflecting state. This state can be made to appear as green, red, blue, or any pre-selected color depending upon the pitch length of the chiral nematic liquid crystal. When a low electric field, e.g. 6 volts per micron of thickness, is applied to the cell, it will switch to a white, light scattering state. In this state, the liquid crystal molecules surrounding the polymer domains have a focal conic texture as a result of the competition of any surface effects, the electric field and the constraint of the polymer domains. The material will remain in the light scattering state when the low electric field is removed. If a higher electric field, e.g. 12 volts per micron of thickness, is applied to the cell, the material becomes optically clear until the voltage is removed. If the electric field is turned off quickly, the material switches to the uniform twisted planar structure which has the pre-selected color dictated by the pitch length. The light reflecting state remains

stable at zero field condition. If the field is turned off slowly, the material changes to its light scattering state which also remains stable at zero field condition. The effect of the polymer domains is to stabilize both the planar and focal conic textures in the zero field condition. The magnitude of the field  
5 necessary to drive the material between various states will, of course, vary depending upon the nature and amount of the particular liquid crystal and polymer used, but could be easily determined by one of ordinary skill in the art in view of the instant disclosure.

In the multistable color displays the chiral nematic liquid crystal has a  
10 pitch length in a preferred range of from about 0.25 to 0.44 microns effective to reflect circularly polarized colored light. Typical pitch lengths are 0.27 microns for blue color, 0.31 microns for green color and 0.40 microns for red color. Multistable color display materials have been prepared containing from about 27 to about 66% chiral material based on the combined weight of nematic liquid  
15 crystal and chiral material. The ranges can vary, however, depending upon the chiral material, liquid crystal and the polymer used.

In one embodiment the multistable display materials can be prepared to function as a bistable light shutter. By adjusting the pitch length of the chiral nematic liquid crystal to reflect light in the ultra violet range, the material will  
20 appear clear when switched to the stable planar texture because the reflected light is outside the visible spectrum. As with the color reflecting cells, the material will scatter light when switched to the stable focal conic texture. Hence, the multistable material can be switched between a stable optically clear state, where the liquid crystal reflects light in the ultra violet range, and a stable light  
25 scattering state. Pitch lengths effective to reflect light in the ultra violet range will typically be from about 0.5 to about 1 micron. Bistable light shutters that reflect light in the ultra violet, and hence appear clear in the planar texture, and scatter light in the focal conic texture have been prepared containing about 18% by weight chiral material based on the combined weight of chiral material and  
30 nematic liquid crystal.

Surprisingly, the multistable color reflecting material exhibits a stable grey scale, i.e., multiple optical states characterized by varying degrees of intensity of reflection, all of which are stable in the absence of an applied field. In between

the reflecting and scattering states the material exhibits stable grey scale reflectance of the colored light depending upon the voltage of the electric field addressing pulse. In each case, the electric field pulse is preferably an AC pulse, and more preferably a square AC pulse, since a DC pulse will tend to cause  
5 ionic conduction and limit the life of the cell.

Accordingly, the invention also features a method of addressing a polymer stabilized chiral nematic liquid crystal material capable of being switched between a color reflecting state that reflects a maximum reference intensity, and a light scattering state exhibiting a minimum reference intensity. The method  
10 comprises applying voltage pulses of varying magnitude sufficient to achieve stable color reflectivity between said maximum and minimum, thereby producing stable grey scale reflectance from the material.

Preferably the method is characterized by subjecting the material to an AC pulse of sufficient duration and voltage to cause a proportion of said chiral  
15 nematic material to exhibit a first optical state and the remaining proportion of the chiral nematic material to exhibit a second optical state that is different than the first state. In the preferred embodiment, the proportion of the material in the first optical state exhibits the planar texture and the remainder of the material in the second optical state exhibits the focal conic texture, the intensity  
20 of reflection being proportional to the amount of the material in the planar reflecting texture.

Many additional features, advantages and a fuller understanding of the invention will be had from the following detailed description of preferred  
25 embodiments and the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagrammatic, cross-sectional illustration of a light modulating cell incorporating the polymer-liquid crystalline material of the invention.

30 Figure 2 is a diagrammatic, fragmentary, enlarged cross-sectional illustration of the new material when the liquid crystal is homeotropically aligned to affect an optically clear state.

Figure 3 is a diagrammatic, fragmentary, enlarged cross-sectional illustration of the material in a light scattering state wherein the liquid crystal in proximity to the polymer domains is homeotropically aligned, while the surrounding liquid crystal has a focal conic texture.

5        Figure 4 is a diagrammatic, fragmentary, enlarged cross-sectional illustration of the material when the liquid crystal has a twisted planar texture.

Figure 5 is a diagrammatic, fragmentary, enlarged cross-sectional illustration of the material wherein the liquid crystal in proximity to the polymer domains has a twisted planar structure, while the surrounding liquid crystal has a focal conic texture.

10        Figure 6 is a plot of the dynamic response of a cell to AC pulses of varying voltages demonstrating grey scale reflection in the voltage range of about 20 and 34 volts.

## 15        DESCRIPTION OF PREFERRED EMBODIMENTS

The diagrammatically illustrated cell in Figure 1 comprises glass plates 10, 11 which are sealed around their edges and separated by spacers 12. As shown, the glass plates 10, 11 are coated with indium-tin oxide or the like to form transparent electrodes 13. The reference character 14 represents an optional rubbed polyimide coating which can be applied to the electrodes in order to affect homogeneous surface alignment of the liquid crystal directors.

20        The cell of Figure 1 is filled with the polymer-liquid crystalline material of the invention. The liquid crystalline light modulating material is generally comprised of phase-separated polymer domains 15 dispersed in surrounding chiral nematic liquid crystal 16 having positive dielectric anisotropy. An AC voltage source 17 is shown connected to the electrodes 13 in order to switch the cell between different optical states.

25        It is to be understood that the form of the cell depicted in Figure 1 has been chosen only for the purpose of describing a particular embodiment and function of the liquid crystalline light modulating material of the invention, and that the material can be addressed in various ways and incorporated in other types of cells. For example, instead of being addressed by externally activated electrodes, the new material can be addressed by an active matrix, a multiplexing



scheme or other type of circuitry, all of which will be evident to those working in the art. Similarly, the cells can be prepared without the optional alignment layers.

5 In accordance with the invention, the polymer domains 15 are defined by polymer which is phase separated from a solution with the chiral nematic liquid crystal. The chiral nematic liquid crystal in proximity to the polymer domains 15 is anchored by the polymer.

10 The polymer content in terms of weight based on the combined weight of chiral nematic liquid crystal and polymer will vary depending upon the polymer used, and is preferably present in an amount ranging from about 1.5 to about 40% by weight based on the combined weight of polymer and liquid crystal. For example, cells have been prepared with a polymer content ranging from about 1.5% to 10% using certain bisacrylates, from about 20 to 30% using certain hydroxy functionalized polymethacrylates, and about 40% when certain epoxies, 15 thermoplastics and U.V. cured polymers are used. It is to be understood, therefore, that the polymer content is subject to some variation, in as much as what constitutes a desirable or undesirable appearance of the cell in its various optical states is a matter of subjective judgment.

20 In a preferred manner of preparing the cell shown in Figure 1, the polymer (or its precursors, e.g. monomers) is dissolved with the chiral nematic liquid crystal together with any necessary photo-initiator, crosslinking or curing agent. The solution is then introduced between the glass plates 10, 11, shown here having the optional rubbed polyimide coatings 14. The solution is then polymerized in situ to induce concomitant phase separation of the polymer to 25 form the polymer domains in the cell, conceptually illustrated by reference character 15. The polymerization of the polymer-liquid crystal solution can take place either in the presence of an electric field effective to homeotropically align the liquid crystal directors or in zero field. In the latter case, the liquid crystal molecules will prefer a twisted planar texture oriented parallel to the cell walls.

30

#### Normal Mode Cells

Normal mode cells which scatter light in a field-OFF condition and are optically clear in a field-ON condition are prepared using a chiral nematic liquid

crystal effective to reflect light outside the visible spectrum, preferably in the infra-red spectrum. A preferred pitch length ranges from about 1.0 to about 4.0 microns. Liquid crystalline light modulating materials having the desired pitch length may contain from about 1 to about 16% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material; although, the weight amounts can vary depending upon the particular liquid crystal, chiral material and polymer which are used.

Normal mode cells are prepared by polymerizing the polymer-liquid crystal solution in the presence of an electric field. As shown in Figure 2, the electric field is effective to untwist the chiral nematic liquid crystal molecules and homeotropically align the liquid crystal directors 20. A single polymer domain 15 is conceptually illustrated in Figure 2.

Each of the polymer domains 15 is believed to be a complex, often cross-linked, three-dimensional network. When the electric field is turned off as illustrated in Figure 3, the liquid crystal in the vicinity of the polymer tends to remain homeotropically aligned because of the anchoring affect of the polymer. The surrounding liquid crystal indicated by reference numeral 30 tends to reform to a focal conic texture, i.e., helically twisted molecules having randomly oriented helical axes. The focal conic texture results from competition between the various forces in the system such as any surface effects and the constraining effect of the polymer domains on the liquid crystal. In the field-OFF condition illustrated in Figure 3, the polymer-liquid crystalline material is strongly light scattering independent of the polarization of incident light.

When the electric field is turned on to homeotropically align the liquid crystal directors as shown in Figure 2, the polymer-liquid crystalline material is optically clear. Because of the typically small amount of polymer in the composition, there is no significant variation or fluctuation of a refractive index throughout the liquid crystalline material. Therefore, the cell incorporating the material is haze-free at all viewing angles, although as the amount of polymer is increased the amount of haze may increase.

#### Example 1

A normal mode cell, light scattering in the field-OFF condition and optically clear in a field-ON condition, was prepared using a solution of chiral nematic liquid crystal containing 8.8% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material, and 2.9% by weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral nematic liquid crystal had a pitch length of about 1.4 microns.

The polymerizable solution consisted of:

- 175.2 mg. of E-31LV nematic liquid crystal mixture;
- 8.3 mg. of 4''-(2-methylbutylphenyl) - 4'-(2-methylbutyl)-4-biphenyl carboxylate (chiral material);
- 8.5 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 5.7 mg. of bisacryloyl biphenyl (BAB lab synthesized monomer);
- 1.0 mg. of benzoin methyl ether (BME photo-initiator).

E-31LV consists essentially of a mixture of: 4 ethyl 4'-cyanobiphenyl, 4-butyl-4'-cyanobiphenyl, 4-hexyl-4'-cyanobiphenyl, 4-methoxy-4'-cyanobiphenyl, 4-propyloxy-4'-cyanobiphenyl, 4-pentyl-4'-cyanoterphenyl and 4-(4'-ethylbiphenyl-4-carbonyloxy) methyl benzene.

A cell having two glass plates sealed at the edges and separated by 8 micron thick Mylar spacers was filled with the polymerizable solution. The glass plates were coated with indium-tin oxide to provide transparent electrodes. The electrodes were coated with polyimide and buffed to affect homogeneous surface alignment of the liquid crystal.

The filled cell was irradiated with U.V. light to polymerize the monomer and cause phase separation of the polymer into polymer domains in the cell. While the cell was being irradiated, an AC electric voltage was applied to cause homeotropic alignment of the liquid crystal.

At zero field, the cell was opaque or light scattering and the transmittance in this state was less than 5%. When an AC voltage ( $V_{rms}=35V$ ) was applied across the cell, it became optically clear. In the field-ON condition, the cell was transparent for incident light at all viewing angles.

Example 2

The following series of normal mode cells were prepared with varying pitch lengths and concentrations of chiral material.

5 A normal mode cell was prepared using a solution of chiral nematic liquid crystal containing 11.1% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material, and 2.9% by weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral nematic liquid crystal had a pitch length of about 1.4 microns.

10 The polymerizable solution consisted of:

144 mg. of E-31LV nematic liquid crystal mixture from EM Industries;

18 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);

4.9 mg. of 4,4'-bisacryloyl biphenyl (monomer); and

15 1.0 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared as in Example 1. An AC electric voltage was applied during polymerization to cause homeotropic alignment of the liquid crystal.

20 At zero field, the cell was opaque or light scattering and the transmittance was less than 5%. When an AC voltage ( $V_{rms}=25V$ ) was applied across the cell, it became optically clear. In the field-ON condition, the cell was transparent for incident light at all viewing angles.

25 A normal mode cell was prepared using a solution of chiral nematic liquid crystal containing 12.9% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material and 3.3% by weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral nematic liquid crystal had a pitch length of about 1.2 microns.

30 The polymerizable solution consisted of:

137 mg. of E-31LV nematic liquid crystal mixture;

20.4 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);

5.3 mg. of 4,4'-bisacryloyl biphenyl (monomer); and

2.4 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared as in Example 1. An AC electric voltage was applied during polymerization to cause homeotropic alignment of the liquid crystal.

At zero field, the cell was opaque or light scattering and the transmittance of the cell was 15%. When an AC voltage ( $V_{rms}=21V$ ) was applied across the cell, it became optically clear. In the field-ON condition, the cell was transparent for incident light at all viewing angles. Because the zero field transmittance was 15%, the cell was marginally effective.

A normal mode cell was prepared using a solution of chiral nematic liquid crystal containing 5.9% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material and 2.2% by weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral nematic liquid crystal had a pitch length of 2.6 microns.

The polymerizable solution consisted of:

- 200 mg. of E-31LV nematic liquid crystal;
- 12.6 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 4.8 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 1.8 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared as in Example 1. An AC electric voltage was applied during polymerization to cause homeotropic alignment of the liquid crystal.

At zero field, the cell was opaque or light scattering and the transmittance of the cell was 62%. When an AC voltage ( $V_{rms}=14V$ ) was applied across the cell, it became optically clear. In the field-ON condition, the cell was transparent for incident light at all viewing angles. Because the zero field transmittance was 62%, the cell was not acceptable.

A normal mode cell was prepared from a polymerizable solution consisting of 0.96% R-1011 chiral material (E. Merck), 94.82% ZLI-4389 nematic liquid crystal mixture (E. Merck), 3.83% BAB6 lab synthesized bisacrylate monomer, and 0.38% BME photo-initiator introduced between glass plates coated with ITO to serve as transparent electrodes. The glass plates were cleaned but did not have any surface treatment for alignment of the liquid

crystal. The thickness of the cell was controlled by 15  $\mu\text{m}$  glass fiber spacers. The sample was irradiated with U.V. light to polymerize the monomer.

This sample had a pitch length of 3.9  $\mu\text{m}$ . In the field-OFF condition the transmittance of the sample was 1.8%. In the field-ON condition the  
5 transmittance was 88%. The contrast ratio was 49:1. The sample had a low drive voltage of  $V_{\text{rms}}=8\text{V}$ . The turn-on and turn-off times were 21 ms and 66 ms, respectively. This cell was acceptable.

Another normal mode cell was prepared just like the preceding cell from a polymerizable solution consisting of 2.16% R-1011 chiral agent, 93.36% ZLI-  
10 4389 nematic liquid crystal mixture, 3.83% BAB6 bisacrylate monomer and 0.38% BME photo-initiator. This sample had a pitch length of 1.74  $\mu\text{m}$ . In the field-OFF condition the transmittance of the cell was 0.37%. In the field-ON condition the transmittance was 87%. The cell had an excellent contrast ratio of 230:1. The drive voltage was 15V and the turn-on and turn-off times were 50 ms  
15 and 14 ms, respectively.

Another normal mode cell was prepared just like the preceding example from a polymerizable solution consisting of 2.62% R-1011 chiral material, 92.62% ZLI-4389 nematic liquid crystal mixture, 4.38% BAB6 bisacrylate monomer and 0.44% BME photo-initiator. This sample had a pitch length of 1.4  
20  $\mu\text{m}$ . In the field-OFF condition the transmittance of the cell was 0.35%. In the field-ON condition the transmittance was 87%. This cell had an excellent contrast ratio of 250:1. The drive voltage was 20V and the turn-on and turn-off times were 37 ms and 25 ms, respectively. It was noted that the drive voltage tends to increase as the pitch length is decreased.

25

### Example 3

The following series of normal mode cells were prepared with varying concentrations of the monomer 4,4'-bisacryloyl biphenyl (BAB).

A normal mode cell was prepared using a solution of chiral nematic liquid  
30 crystal containing 10.0% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material, and 4.4% by weight of a cross-linking monomer based on the combined weight of chiral liquid crystal and

monomer. The chiral nematic liquid crystal had a pitch length of about 1.5 microns.

The polymerizable solution consisted of:

- 107 mg. of E-31LV nematic liquid crystal;
- 5 11.91 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 5.5 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 1.7 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared as in Example 1. An AC electric field was applied during polymerization to cause homeotropic alignment of the liquid crystal.

- 10 At zero field, the cell was opaque or light scattering and the transmittance was 7%. When an AC voltage ( $V_{rms}=28V$ ) was applied across the cell, it became optically clear. In the field-ON condition, the cell was transparent for incident light at all viewing angles. This cell had good contrast between the field-ON and field-OFF states.

- 15 Another normal mode cell was prepared using a solution of chiral nematic liquid crystal containing 9.9% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material and 1.2% by weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral nematic liquid crystal had a pitch length of
- 20 about 1.5 microns.

The polymerizable solution consisted of:

- 164 mg. of E-31LV nematic liquid crystal; -
- 18 mg. 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 2.2 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 25 .7 mg. benzoin methyl ether (photo-initiator).

The cell was prepared as in Example 1. An AC electric field was applied during polymerization to cause homeotropic alignment of the liquid crystal.

- At zero field, the transmittance was 67%. When an AC voltage ( $V_{rms}=18V$ ) was applied across the cell, it became optically clear. In the field-
- 30 ON condition, the cell was transparent for incident light at all viewing angles. Because the zero field transmittance was 67%, the cell was not acceptable.

A normal mode cell was prepared using a solution of chiral nematic liquid crystal containing 9.8% by weight chiral material based on the combined weight

of nematic liquid crystal and chiral material and 9.0% by weight monomer based on the combined weight of chiral liquid crystal and monomer. The chiral liquid crystal had a pitch length of about 1.5 microns.

The polymerizable solution consisted of:

- 5           101 mg. of E-31LV nematic liquid crystal;
- 11.0 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 11.4 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 3.5 mg. of benzoin methyl ether (photo-initiator).

10       The cell was prepared as in Example 1. The cell was almost transparent at zero field and was not a good cell.

#### Example 4

A normal mode cell without any surface aligning layer was prepared from a polymerizable solution consisting of 2.18% R-1011 chiral material (E. Merck),  
15   94.14% ZLI-4389 nematic liquid crystal (E. Merck), 2.90% BAB6 lab synthesized bisacrylate monomer, and .29% BME photo-initiator. The mixture was introduced between glass plates having ITO transparent electrodes. The thickness of the cell was controlled by 15  $\mu$ m glass spacers. The glass plates were cleaned but did not have any surface treatments for alignment of the liquid  
20   crystal. The sample was irradiated with U.V. light to polymerize the monomer.

The sample required a drive voltage of 18V. The turn-ON time was 52 ms and the turn-OFF time was 19 ms. The contrast ratio was 1:245 and the transmission in the field-ON condition was 90%.

25

#### Reverse Mode Cells

Reverse mode cells which are optically clear in a field-OFF condition and light scattering in a field-ON condition are prepared using a chiral nematic liquid crystal having a pitch length outside the visible spectrum, preferably in the infra-red spectrum. In the case of reverse mode cells, the pitch length varies from  
30   about 1.0 to about 4.0 microns. The chiral nematic liquid crystal typically consists of from about 1 to about 16% by weight chiral material based on the combined weight of nematic liquid crystalline chiral material; although, the



weight amounts can vary depending upon the particular liquid crystal, chiral material and polymer which are used.

Reverse mode cells are made by polymerizing the polymer-liquid crystal solution at zero field. As shown in Figure 4, the liquid crystal molecules throughout the material prefer a twisted planar texture represented by reference numeral 40. A single polymer domain is again conceptually represented at 15. In the field-OFF condition shown in Figure 4, a polymer-liquid crystalline material is optically clear, since there is no reflecting or scattering of light in the visible spectrum.

10 In the field-ON condition conceptually shown in Figure 5, the liquid crystal molecules in the vicinity of the polymer domains 15 prefer the twisted planar orientation because of the anchoring affect of the polymer domains. The surrounding liquid crystal is reformed by the electric field to a focal conic texture. The focal conic texture in the presence of the field is a result of  
15 competition between the forces in the system such as any surface effects, the electric field and the constraint of the polymer domains. In the field-ON condition of Figure 5, the liquid crystalline-polymer material is strongly light scattering for all polarizations of incident light.

20

#### Example 5

A reverse mode cell, light scattering in the field-ON condition and optically clear in a field-OFF condition, was prepared using a solution of chiral nematic liquid crystal containing 4.0% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material, and 4.6% by  
25 weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral nematic liquid crystal had a pitch length of about 3.7 microns.

The polymerizable solution consisted of:

30 107 mg. of E-31LV nematic liquid crystal;  
4.5 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);  
5.5 mg. of 4,4'-bisacryloyl biphenyl (monomer); and  
1.2 mg. of benzoin methyl ether (photo-initiator).

A cell having two glass plates sealed at the edges and separated by 8 micron thick Mylar spacers was filled with the polymerizable solution. The glass plates were coated with indium-tin oxide to provide transparent electrodes. The electrodes were coated with polyimide and buffed to affect homogeneous surface alignment of the liquid crystal. The filled cell was irradiated with U.V. light to polymerize the monomer and cause phase separation of the polymer into polymer domains in the cell.

At zero field, the cell was optically clear and transparent for incident light at all viewing angles. In the field-OFF state the transmittance was 93%. When an AC voltage ( $V_{rms}=27V$ ) was applied across the cell, it became opaque or light scattering. In the field-ON state, the transmittance was 8%, independent of the polarization of the incident light.

#### Example 6

A series of reverse mode cells were made with varying pitch lengths and concentrations of chiral materials.

A reverse mode cell was prepared using a solution of chiral nematic liquid crystal containing 7.8% by weight chiral material based on the weight of nematic liquid crystal and chiral material and 4.7% by weight of a cross-linking monomer based on the weight of chiral liquid crystal and monomer. The chiral nematic liquid crystal had a pitch length of about 1.9 microns.

The polymerizable solution consisted of:

- 159 mg. of E-31LV nematic liquid crystal;
- 13.7 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 8.5 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- .8 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared in the manner described in Example 5.

At zero field, the cell was optically clear and transparent for incident light at all viewing angles. In the field-Off state the transmittance was 98%. When an AC voltage ( $V_{rms}=30V$ ) was applied, the cell became opaque or light scattering. In the field-ON state, the transmittance was 9% and was independent of the polarization of the incident light.

A reverse mode cell was prepared using a solution of chiral nematic liquid crystal containing 12.1% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material and 4.8% by weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral nematic liquid crystal had a pitch length of about 1.3 microns.

The polymerizable solution consisted of:

- 129 mg. of E-31LV nematic liquid crystal;
- 17.7 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 7.5 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- .6 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared in the manner described in Example 5.

At zero field, the cell was optically clear and transparent for incident light at all viewing angles. In the field-OFF state the transmittance was 96%. When an AC voltage ( $V_{rms}=41V$ ) was applied, the cell became opaque or light scattering. In the field-ON state, the transmittance was 5%, independent of the polarization of the incident light.

A reverse mode cell was prepared using a solution of chiral nematic liquid crystal containing 1.39% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material and 4.5% by weight of a cross-linking monomer based on the combined weight of monomer and chiral liquid crystal. The chiral nematic liquid crystal had a pitch length of about 10.7 microns.

The polymerizable solution consisted of:

- 263 mg. of E-31LV nematic liquid crystal;
- 3.7 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 12.5 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 1.4 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared in the manner described in Example 5.

At zero field, the cell was optically clear and transparent for incident light at all viewing angles. In the field-OFF state the transmittance was 92%. When an AC voltage ( $V_{rms}=32V$ ) was applied, the transmittance of polarized light parallel to the buffing direction was 35%. When an AC voltage ( $V_{rms}=18V$ ) was

applied, the transmittance of polarized light perpendicular to the buffing direction was 6%.

5 A reverse mode cell was prepared using a solution of chiral nematic liquid crystal containing 16.3% by weight chiral material based on the weight of nematic liquid crystal and chiral material and 4.4% by weight of a cross-linking monomer based on the weight of monomer and liquid crystal. The chiral nematic liquid crystal had a pitch length of about .9 microns.

The polymerizable solution consisted of:

- 10 125.7 mg. of E-31LV nematic liquid crystal;  
24.4 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);  
6.9 mg. 4,4'-bisacryloyl biphenyl (monomer); and  
.7 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared in the same manner as Example 5.

15 At zero field, the cell was optically clear and transparent for incident light at all viewing angles. In the field-Off state the transmittance was 94%. When an AC voltage ( $V_{rms}=50V$ ) was applied, the cell became opaque or light scattering. In the field-ON state, the transmittance was 11% and was independent of the polarization of the incident light. This cell also displayed an hysteresis effect as the cell was switched from the field-ON to field-OFF state.

20

#### Example 7

The following series of reverse mode cells were prepared with varying polymer concentrations.

25 A reverse mode cell was prepared using a solution of chiral nematic liquid crystal containing 6.1% by weight chiral material based on the combined weight of chiral material and nematic liquid crystal and 2.1% by weight of a cross-linking monomer based on the combined weight of monomer and chiral nematic liquid crystal. The chiral nematic liquid crystal had a pitch length of about 2.5 microns.

30 The polymerizable solution consisted of:

- 181 mg. of E-31LV nematic liquid crystal;  
11.7 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);  
4.2 mg. of 4, 4'-bisacryloyl biphenyl (monomer); and

.9 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared in the manner described in Example 5.

At zero field, the cell was optically clear and transparent for incident light at all viewing angles. In the field-OFF state the transmittance was 97%. When an AC voltage ( $V_{rms}=18V$ ) was applied, the cell became opaque or light scattering. In the field-ON state, the transmittance was 14%, and independent of the polarization of the incident light. The turn-off time for this cell was 5 milliseconds.

A reverse mode cell was prepared using a solution of chiral nematic liquid crystal material containing 6% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material, and 2.9% by weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral nematic liquid crystal has a pitch length of about 2.5 microns.

15           The polymerizable solution consisted of:

181 mg. of E-31LV nematic liquid crystal;  
11.5 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);  
5.7 mg. of 4,4'-bisacryloyl biphenyl (monomer); and  
.7 mg. of benzoin methyl ether (photo-initiator).

20 The cell was prepared in the same manner described in Example 5.

At zero field, the cell was optically clear and transparent for incident light at all viewing angles. In the field-OFF state the transmittance was 95%. When an AC voltage ( $V_{rms}=21V$ ) was applied, the cell became translucent or light scattering. In the field-ON state, the transmittance was 8% and independent of the polarization of the incident light. The turn-off time for the cell was 4 milliseconds.

A reverse mode cell was prepared using a solution of chiral nematic liquid crystal containing 6.0% by weight chiral material based on the combined weight of the nematic liquid crystal and chiral material, and 4.3% by weight of a cross-linking monomer based on the combined weight of monomer and chiral liquid crystal. The chiral nematic liquid crystal has a pitch length of about 2.5 microns.

The polymerizable solution consisted of:

180 mg. of E-31LV nematic liquid crystal;

11.5 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);  
8.6 mg. of 4, 4'-bisacryloyl biphenyl (monomer); and  
.9 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared in the manner described in Example 5.

5 At zero field, the cell was optically clear and transparent for incident light at all viewing angles. In the field-OFF state the transmittance was 95%. When an AC voltage ( $V_{rms}=28V$ ) was applied, the cell became translucent or light scattering. In the field-ON state, the transmittance was 8% and independent of the polarization of the incident light. The turn-off time of the cell was 3  
10 milliseconds.

A reverse mode cell was prepared using a solution of chiral nematic liquid crystal containing 6.1% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material, and 5.8% by weight of a cross-linking monomer based on the combined weight of chiral liquid crystal and  
15 monomer. The chiral nematic liquid crystal had a pitch length of about 2.5 microns.

The polymerizable solution consisted of:

179 mg. of E-31LV nematic liquid crystal;  
11.7 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);  
20 10.6 mg. of 4, 4'-bisacryloyl biphenyl (monomer); and  
1.2 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared in the manner described in Example 5.

At zero field, the transmittance was 76%. When the AC voltage ( $V_{rms}=28V$ ) was applied across the cell, the transmittance decreased. In the  
25 field-ON state, the transmittance was 46%.

A reverse mode cell was prepared using a solution of chiral nematic liquid crystal containing 6.0% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material and 1.0% by weight of a cross-linking monomer based on the combined weight of the chiral nematic liquid  
30 crystal and monomer. The chiral nematic liquid crystal had a pitch length of about 2.5 microns.

The polymerizable solution consisted of:

184 mg. of E-31LV nematic liquid crystal;

11.7 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);  
20 mg. of 4,4'-bisacryloyl biphenyl (monomer); and  
.7 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared in the manner described in Example 5.

5        At zero field, the cell was optically clear and transparent for incident light at all viewing angles. In the field-OFF state the transmittance was 96%. When an AC voltage ( $V_{rms}=14V$ ) was applied across the cell, the cell became translucent or light scattering. In the field-ON state, the transmittance was 13%, independent of the polarization of the incident light. The turn-off time was 20  
10        milliseconds, which is long. The cell was also easily damaged by the electric field.

#### Example 8

A reverse mode cell was prepared as in the preceding examples consisting  
15        of two glass plates separated by  $10\mu m$  spacers filled with a polymerizable solution consisting of 94.53% ZLI-4389 nematic liquid crystal (E. Merck), 1.25% ZLI-4572 chiral material (E. Merck), 3.83 BP6DA lab synthesized monomer, and 0.38% photo-initiator. The glass slides were coated with ITO electrodes and rubbed polyimide for homogeneous surface alignment of the liquid crystal. The  
20        material was then polymerized by U.V. irradiation for 2 hours.

In the field-OFF condition the transmittance was 85%. Upon application of a field the transmittance decreased, reaching a minimum transmittance of 10% at 15 volts. When the applied voltage was decreased the material returned to the original transmitting state.

25

#### Example 9

A reverse-mode cell was prepared without a polyimide alignment layer as a surface treatment on the cell walls. The polymer stabilized liquid crystal material was prepared from 94.54% ZLI-4389 nematic liquid crystal mixture,  
30        1.25% ZLI-4572 chiral agent, 3.83% lab synthesized bisacrylate monomer BP6DA, and 0.38% BME photo-initiator and introduced between two glass slides separated by  $15\mu m$  glass fiber spacers as in the previous examples. The glass slides were coated with ITO electrodes, but had no other surface treatment

except cleaning. The cell was filled by capillary action in a vacuum chamber. The sample was irradiated by UV light for 2 hours to polymerize the monomer.

In the field-OFF condition the transmittance was 18%. When an external electric voltage was applied to the cell, the transmittance of the cell decreased.

5 A minimum value of 2% was reached when the voltage was increased to 20V. When the voltage was decreased, the material transformed back to its original texture and the transmittance of the cell increased, although the dynamic response of the cell was comparatively slow.

10

#### Multistable Color Display Cells

The multistable color display material of the invention exhibits a stable grey scale phenomenon characterized by the ability of the material to reflect indefinitely any selected intensity of light between the intensity reflected by the reflecting state and that reflected by the scattering state. When the material is in  
15 the reflecting state the chiral material assumes a planar texture which reflects colored light at a maximum intensity for a given material, the color of the reflected light being determined by the pitch length of the chiral material. An electric field pulse of an appropriate threshold voltage, typically in the range of about 4 to 5 volts per micrometer of thickness, will cause at least a portion of  
20 the material to change its optical state and the intensity of reflectivity to decrease. If the AC pulse is high enough, e.g., in the range of about 6 to 8 volts per micrometer of thickness, the optical state of the material will change completely to the scattering state in which the chiral material exhibits a focal conic texture which reflects light at a minimum intensity for a given material. In  
25 between the reflecting state, which for a given material can be considered to define the maximum intensity of reflectivity for that material, and the scattering state, which can be considered to define the minimum intensity of reflectivity, the intensity of reflectivity ranges along a grey scale, which is simply a continuum of intensity values between that exhibited by the reflecting and scattering states. By  
30 pulsing the material with an AC pulse of a voltage below that which will convert the material from the reflecting state to the scattering state, or visa versa, one obtains an intensity of reflectivity in this grey scale range.



While not wanting to be bound by theory, it has been observed that the intensity of reflectivity along the grey scale is approximately linearly proportional to the voltage of the pulse. By varying the voltage of the pulse the intensity of reflectivity of a given color can be varied proportionally. When the electric field is removed the material will reflect that intensity indefinitely. It is believed that pulses within this grey scale voltage range cause a proportion of the material to convert from the planar texture characteristic of the reflecting state, to the focal conic texture characteristic of the scattering state. Since both the planar texture of the reflecting state and the focal conic texture of the scattering state are stabilized by the polymer in the zero field condition, the grey scale intensities reflected by the display are also stable since the material in these optical states simply comprises a combination of both the stable planar texture and the stable focal conic texture. The intensity of reflectivity along the grey scale is proportional to the amount of chiral material switched from the planar texture to the focal conic texture, or vice versa, which is in turn proportional to the voltage of the AC pulse.

Multistable color display cells which scatter light in one state and reflect circularly polarized colored light in another state with stable grey scale reflection therebetween, and which also can be operated to exhibit optical transparency, are made using chiral nematic liquid crystal which has a pitch length effective to reflect light in the visible spectrum. Preferred materials have a pitch length ranging from about 0.25 to about 0.44 microns. Typical pitch lengths are 0.27 microns for blue color, 0.31 microns for green colors and 0.40 microns for red color. Multistable color display materials have been prepared to contain from about 27 to about 66% chiral material based on the combined weight of nematic liquid crystal and chiral material; although, as in the case of previously described embodiments, the weight amount can vary depending upon the particular chiral material, nematic liquid crystal and polymer which are used.

Figure 4 conceptually illustrates a single polymer domain of the multistable color display material of the invention in its light reflecting state. In this state, the chiral liquid crystal molecules are oriented in a twisted planar structure parallel to the cell walls. Because of the twisted planar texture the material will reflect light, the color of which depends upon the particular pitch

length. In this stable reflecting state, the material exhibits maximum reflectivity that constitutes a maximum reference intensity below which the grey scale intensities are observed.

5 The planar texture of the liquid crystal in the vicinities of the polymer domains 15 is stabilized by the polymer. The surrounding liquid crystal indicated by reference numeral 50 in Figure 5, being less stabilized, tends to reform to the focal conic texture when an AC voltage pulse is applied to the cell. As conceptually illustrated in Figure 5, the multistable color display material is in its light scattering state. In this stable scattering state the material exhibits its  
10 minimum intensity of reflection (i.e., maximum scattering) which defines a minimum reference intensity of reflectivity above which the grey scale intensities are observed.

If the pitch length of the polymer stabilized liquid crystal material is in the range effective to reflect visible light, both the light reflecting state of Figure 4  
15 and the light scattering state of Figure 5, as well as the grey scale states therebetween, are stable in the absence of an electric field. If the multistable material is in the light reflecting state of Figure 4 and a low electric field pulse is applied, for example, about 6 volts per micron, the material will be driven to the light scattering state of Figure 5 and will remain in that state at zero field. If the  
20 multistable material is in the light scattering state of Figure 5 and a higher electric field pulse sufficient to untwist the chiral molecules is applied, e.g., about 10 volts per micron of thickness, the liquid crystal molecules will reform to the light reflecting state of Figure 4 at the end of the pulse and will remain in that condition. It is to be understood that the voltages per micron necessary to drive  
25 the material between optical states may vary depending on the composition of the material, but that the determination of necessary voltages is well within the skill in the art in view of the instant disclosure.

If the pitch length of the liquid crystal material is in the range effective to reflect light in the ultra violet range, a variant of multistable cell can be prepared  
30 which functions as a bistable light shutter. When the material is in the stable planar texture the cell appears clear because the light reflected from the cell is outside the visible spectrum. As with the color reflecting cells, the material will scatter light when switched to the stable focal conic texture. Hence, the

multistable material can be switched between a stable optically clear state, where the liquid crystal reflects light in the ultra violet range, and a stable light scattering state. Pitch lengths effective to reflect light in the ultra violet range will typically be from about 0.5 to about 1 micron. Bistable light shutters that  
5 reflect light in the ultra violet, and hence appear clear in the planar texture, and scatter light in the focal conic texture have been prepared containing about 18% chiral material based on the combined weight of chiral material and nematic liquid crystal.

If the high electric field necessary to untwist the liquid crystal molecules in  
10 the multistable color display materials is maintained, the liquid crystal directors will be homeotropically aligned so that the material is transparent. If the field is slowly removed, the liquid crystal orientation will reform to the light scattering state of Figure 5. When the field is quickly removed, the orientation will reform to the light reflecting state of Figure 4. The intensities of reflectivity reflected  
15 between the reflecting state of Figure 4 and the scattering state of Figure 5 are stable grey scale reflectivities. Of course, the intensity value of the reflecting and scattering states may vary as the composition of the material varies, but the grey scale is defined by the range of intensities therebetween.

At voltages less than that which will transform the material from the  
20 reflecting state of Fig. 4 to the scattering state of Fig. 5, grey scale states which are themselves stable at zero field are obtained. The reflection from the material in these grey scale states is stable because a proportion of the material is in the planar reflecting texture of Fig. 4 and a proportion of the material is in the focal conic scattering texture of Fig. 5, both of which are stabilized by the  
25 polymer in the absence of a field.

Thus, for example, if the material is in the reflecting state of Fig. 4 and an electric field pulse is applied having a voltage insufficient to drive all of the liquid crystal 16 surrounding the polymer domains 15 into the focal conic texture shown at 50 in Figure 5, i.e., insufficient to drive the material completely to the  
30 scattering state, the material will reflect colored light of an intensity that is proportional to the amount of material that remains in the planar reflecting texture. The reflectivity will thus be lower than that reflected from the material when all of the chiral material is in the planar reflecting texture, but still higher

than when switched completely to the focal conic scattering texture. As the voltage of the electric field pulse is increased, more of the chiral material is switched from the planar reflecting texture to the scattering focal conic texture and the reflectivity decreases further until the voltage of the pulse is increased to the point where the material is completely switched to the scattering state. If the voltage of the pulse is increased still further, the intensity of reflection begins to increase again until the magnitude of the pulse is sufficient to untwist the chiral molecules so that they will again reform to the planar light reflecting texture when the pulse is removed and the material is again in the light reflecting state of Figure 4.

If the material is in the focal conic scattering state of Figure 5, an applied electric field pulse will have a negligible effect on the reflectivity of the cell until it reaches a magnitude sufficient to untwist the chiral material, whereby it will reform to the light reflecting state of Figure 4, as described above, when the field is removed. The grey scale response of a cell as described above is illustrated in Figure 6 which shows the response of the material prepared in Example 10 to varying pulse voltages.

#### Example 10

A multistable grey scale display cell was made from a polymer stabilized chiral nematic liquid crystalline material of the following components:

- 160.7 mg - CB15 cholesteric liquid crystal, BDH Chemicals
- 160.7 mg - CE2 cholesteric liquid crystal, BDH Chemicals
- 488.8 mg - E31 nematic liquid crystal, BDH Chemicals
- 8.0 mg - BAB (4,4'-bisacryloylbiphenyl), lab synthesized monomer
- 3.0 mg - BME (benzoinmethyl ether), Polyscience Co., photo-initiator
- 2.2 mg - R4, dichroic dye

A mixture of the liquid crystal and monomer was sandwiched between two glass plates with ITO electrodes. The glass plates were polyimide coated and buffed for homogeneous alignment of the liquid crystal. The back plate was painted black and separated from the front plate by 5  $\mu$ m glass fibers. In the reflecting state the cell reflected green color. In the scattering state the cell was

black. The filled cell was irradiated with U.V. light for thirty minutes to polymerize the monomer and cause phase separation of the polymer into phase separated polymer domains in the cell.

The reflectivity of the cell in response to AC pulse of varying voltages was measured. In the measurement, square AC pulses of width of 10 milliseconds (ms) were used. For this material an applied pulse of 34V switched the cell completely into the scattering state, independent of whether it was in the reflecting state or the scattering state before the pulse. Minimum reflection is observed here. An applied pulse of 50V switched the cell into the reflecting state independent of whether the cell was in the scattering or reflecting state prior to the pulse. Maximum reflection is observed here. The transformation from the reflecting to the scattering state was near 0.5ms. The transformation from the scattering to the reflecting state was near 300ms.

The grey scale response of the cell in response to pulses of varying voltage is seen in Fig. 6. Here the voltage of the pulse was varied and the reflection of the cell was measured one second after the pulse. Curve A is the response of the cell when the material is in the reflecting state prior to each pulse. Prior to each pulse plotted on curve A the material was subjected to a high AC pulse of about 50V to ensure that it was completely in the reflecting state prior to the pulse. When the voltage of the pulse is below 20V, the reflection of the cell is not affected. When the voltage of the pulse is between 20V and 34V, the later being the voltage necessary to switch the cell to the scattering state, the reflectivity of the cell decreases approximately linearly as the voltage of the pulse is increased. Grey scale reflectivity is observed in this voltage range. In each case the material continued to reflect after the pulse was removed. When the voltage of the pulse was increased above 34V, the reflectivity of the cell increased until the reflectivity reached its original value, i.e., that of the reflecting state, above 46V. Curve B is the response of the cell when the material was initially in the scattering state prior to the AC pulse. Here the reflectivity of the cell remains unchanged for an AC pulse below 40V. Above 40V the material switched to the reflecting state.

Example 11

A color display cell reflecting red circularly polarized light in the reflecting state was prepared using a solution of chiral nematic liquid crystal containing 29.8% by weight chiral material based on the combined weight of chiral material and nematic liquid crystal, and 2.7% by weight of a cross-linking monomer based on the combined weight of monomer and chiral liquid crystal. The chiral liquid crystal had a pitch length of .41 microns.

The polymerizable solution consisted of:

- 67.8 mg. of E-31LV nematic liquid crystal;
- 14.0 mg. of 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl carboxylate (chiral material);
- 14.8 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 2.7 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 1.0 mg. of benzoin methyl ether (photo-initiator).

A cell having two glass plates sealed at the edges and separated by 8 micron thick Mylar spacers was filled with the polymerizable solution. The glass plates were coated with indium-tin oxide to provide transparent electrodes. The electrodes were coated with polyimide and buffed to affect homogeneous surface alignment of the liquid crystal.

The filled cell was irradiated with U.V. light for thirty minutes to polymerize the monomer and cause phase separation of the polymer into phase separated polymer domains. Upon the application of a high AC voltage pulse, about 104V, the cell was optically clear and transparent to incident light. When the pulse was removed the cell was in the stable planar reflecting state. An AC pulse between about 50 and 85V switched the cell to a stable focal conic scattering state. Both the reflecting and scattering states were stable at zero field for over several months.

Example 12

A cell having a blue reflecting state was prepared using a solution of chiral nematic liquid crystal containing 45.3% by weight chiral material based on the weight of chiral material and nematic liquid crystal, and 1.5% by weight of a cross-linking monomer based on the combined weight of monomer and chiral

nematic liquid crystal. The chiral nematic liquid crystal had a pitch length of about .27 microns, reflecting blue circularly polarized light in the reflecting state.

The polymerizable solution consisted of:

- 132.6 mg. of E-31LV nematic liquid crystal;
- 5 50.0 mg. of 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl carboxylate (chiral material);
- 59.7 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 3.7 mg. of 4, 4'-bisacryloyl biphenyl (monomer); and
- 1.0 mg. of benzoin methyl ether (photo-initiator).

- 10 The cell was prepared as in Example 11. The cell was in a blue reflecting state after the removal of the high voltage pulse.

#### Example 13

- 15 A cell having a green reflecting state was prepared using a solution of chiral nematic liquid crystal containing 39.1% by weight chiral material based on the weight of chiral material and nematic liquid crystal and 2.0% by weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral liquid crystal had a pitch length of about .31 microns, reflecting green circularly polarized light.

- 20 The polymerizable solution consisted of:

- 85.6 mg. of E-31LV nematic liquid crystal;
- 27.0 mg. of 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl carboxylate (chiral material);
- 28.0 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 25 2.9 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 1.0 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared as in the preceding examples. The cell was in a green reflecting state after the removal of the high voltage pulse.

30

#### Example 14

A cell having a red reflecting state was prepared using a solution of chiral nematic liquid crystal containing 30.0% by weight chiral material based on the combined weight of chiral material and nematic liquid crystal and 1.9% by weight

of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral liquid crystal has a pitch length of about .41 microns.

The polymerizable solution consisted of:

- 5 80.0 mg. of E-31LV nematic liquid crystal;
- 16.7 mg. of 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl  
carboxylate (chiral material);
- 17.5 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 22 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 10 1.0 mg. of benzoin methyl ether (photo-initiator).

The sample cell was prepared as in the preceding examples. The cell was a red reflecting state after removal of the high voltage pulse.

#### Example 15

- 15 A green reflecting cell with a greater degree of contrast between the reflecting state and scattering state was prepared using a solution of chiral nematic liquid crystal containing 39.1% by weight chiral material based on the combined weight of chiral material and nematic liquid crystal and 2.0% by weight of a cross-linking monomer based on the combined weight of monomer and
- 20 chiral nematic liquid crystal. The chiral nematic liquid crystal had a pitch length of about .31 microns, reflecting green circularly polarized light.

The polymerizable solution consisted of:

- 85.6 mg. of E-31LV nematic liquid crystal;
- 27.0 mg. of 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl  
25 carboxylate (chiral material);
- 28.0 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 2.7 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 1.0 mg. of benzoin methyl ether (photo-initiator).

- A cell having two glass plates sealed at the edges and separated by 8
- 30 micron thick Mylar spacers was filled with the polymerizable solution. The glass plates were coated with indium-tin oxide to provide transparent electrodes. The electrodes were coated with polyimide and buffed to affect homogeneous surface alignment of the liquid crystal.



The filled cell was irradiated with U.V. light to polymerize the monomer and cause phase separation of the polymer into polymer domains. While the cell was being irradiated, an AC electric voltage was applied to cause homeotropic alignment of the liquid crystal.

- 5        The state of the cell was controlled by the voltage of an electric pulse. When a high AC voltage ( $V_{rms} = 104V$ ) was applied, the cell was optically clear and transparent to all angles of incident light. When the high AC voltage was removed, the sample was in the reflecting state and because of the pitch of the chiral liquid crystal, the color of the cell was green. When an AC voltage ( $50V$   
10  $\leq V_{rms} \leq 85V$ ) was applied the cell switched to the light scattering state and after removal of the low voltage field the cell remained in the light scattering state. Both the reflecting and scattering states were observed to be stable states. This cell appeared to have better contrast between the reflecting and scattering states than the cell prepared in the preceding examples. This should result in a  
15 broader grey scale obtainable by this material.

#### Example 16

- A cell was prepared where no monomer was added to the chiral nematic liquid crystal. The solution of chiral nematic liquid crystal contained 32.4% by  
20 weight chiral material based on the combined weight of chiral material and nematic liquid crystal.

The solution consisted of:

- 121.6 mg. of E-31LV nematic liquid crystal;  
29.7 mg. of 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl  
25 carboxylate (chiral material); and  
20.5 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material).

- A cell having two glass plates sealed at the edges and separated by 10 micron thick Mylar spacers was filled with the chiral nematic liquid crystal solution. The glass plates were coated with indium-tin oxide to provide  
30 transparent electrodes. The electrodes were coated with polyimide and buffed to affect homogeneous surface alignment of the liquid crystal.

At zero field, the scattering state changed into the reflecting state over a time span of one hour. The reflecting state of this cell was not uniform as well.

Example 17

A multistable cell was prepared using a solution of chiral nematic liquid crystal containing 29.8% by weight chiral material based on the combined weight of chiral material and nematic liquid crystal and 2.7% by weight of a cross-linking monomer based on the combined weight of chiral nematic liquid crystal and monomer. The chiral nematic liquid crystal had a pitch length of about .41 microns.

The polymerizable solution consisted of:

- 67.8 mg. of E-31LV nematic liquid crystal;
- 14.0 mg. of 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl carboxylate (chiral material);
- 14.8 mg. of 4-cyano-4'-(2-methyl)-butylbiphenyl (chiral material);
- 2.7 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- 1.0 mg. of benzoin methyl ether (photo-initiator).

The cell was prepared in the manner described in Example 11. The cell in the reflecting state was red after the removal of the high voltage pulse. The voltages required to switch the cell to the reflecting or scattering states were the same as in Example 11. The reflecting state and scattering state had good contrast and both states were stable.

A multistable cell was prepared using a solution of chiral nematic liquid crystal containing 30.3% by weight chiral material based on the combined weight of chiral material and nematic liquid crystal and 6.9% by weight of a cross-linking monomer. The chiral nematic liquid crystal had a pitch length of about .40 microns.

The polymerizable solution consisted of:

- 92.8 mg. of E-31LV nematic liquid crystal;
- 20.0 mg. of 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl carboxylate (chiral material);
- 20.3 mg. of 4-cyano-4'-(2-methyl) butylbiphenyl (chiral material);
- 9.9 mg. of 4,4'-bisacryloyl biphenyl (monomer); and
- .8 mg. of benzoin methyl ether (photo-initiator).

The sample cell was prepared in the manner described in Example 11. The cell did not have a scattering state. Following removal of any AC electric

pulse, the sample cell returned to the reflective state. The color of the cell in the reflective state was red.

#### Example 18

5           A cell according to the invention was prepared using an epoxy. The epoxy was composed of, by weight, 6.1% Epon 828, 22.5% Capcure 3-800, 11.4% Heloxy 97. The epoxy was combined with 60% liquid crystal composed of a mixture of 57.1% E7 (nematic liquid crystal mixture), 21.4% CB15 (chiral material), and 21.5% CE2 (chiral material). The materials were hand mixed for  
10   5 minutes. A homogeneous solution was formed by heating the mixture to 90°C and stirring. The resulting mixture was sandwiched between ITO coated glass plates with 10  $\mu$ m spacers. The resulting assembly was cured in a 90°C oven overnight. The resulting shutter can be switched from a focal conic to planar texture by application of a 175 volt pulse and then back to the focal conic  
15 texture by application of an 80 volt pulse. Both the planar and focal conic texture are stable with multiple stable reflecting states, i.e., stable grey scale, therebetween. Advantageously, this film is self supporting and self adhering in that the material itself seals the plates together.

#### Example 19

20           Another light modulating cell was prepared from an optical adhesive U.V. cured polymer. A liquid crystal mixture comprising 57.1% E7, 21.4% CB15, and 21.5% CE2 was mixed with 25% by weight Norland Optical Adhesive NOA65. The solution was heated to about 100°C to form a homogeneous solution of  
25 liquid crystal and polymer. The resulting mixture was sandwiched between two transparent conducting glass substrates with 20  $\mu$ m spacers to control thickness and then cured by U.V. light for 5 minutes under an Oriel 450 watt Xenon arc lamp. The sandwich was kept in a 100°C oven until immediately prior to U.V. curing. Upon the application of an appropriate field the resulting shutter was  
30 switched between stable focal conic and planar textures, respectively, with multiple stable grey scale states therebetween. As with the preceding example, this film was also advantageously self supporting.

Example 20

Several additional cells were prepared using various mixtures of E48 as the nematic liquid crystal. In these cells the chiral material was comprised of TM74A or various mixtures of CB15 and CE2 in amounts ranging from 10 to 45% of the liquid crystal component. The polymer AU1033 (a hydroxy functionalized polymethacrylate) was used in these cells in amounts ranging from 20-30% by weight based on the combined weight of the liquid crystal mixture and polymer. A diisocyanate crosslinking agent (N75) was added to the solutions of liquid crystal and polymer and the solutions incorporated into a 10  $\mu\text{m}$  thick cells. Upon evaporation of the solvent the materials were thermally cross linked at 100°C. The resulting shutters were all in a stable planar texture and could be switched to a stable focal conic texture upon the application of a field. Application of a higher field switched the shutters back to the planar texture.

Additional cells were made using E7 and E31 as the nematic host with 45% chiral additive selected from TM74A or mixtures of CE2 and CB15 and 30% AU1033 as the polymer binder. These shutters were also switchable between stable planar and focal conic textures.

Example 21

More shutters were prepared using a chiral nematic liquid crystal comprised of various mixtures of E48, CB15 and CE2, and TM74A in 5 and 10% PMMA polymer. The mixtures were poured onto conducting glass substrates and the solvent allowed to evaporate. Spacers were used to produce a final film thickness of 10  $\mu\text{m}$ . The film was heated to 100°C and a second substrate was added to form the cell. The resulting shutters reflected blue light in the planar reflecting texture. As with the other shutters, the materials switched to a stable focal conic texture upon application of a field and then back to a stable planar texture upon application of a higher field. These cells were also advantageously self sustaining.

Example 22

A multistable color reflecting cell was prepared as in the preceding examples from a material of the following components:

- 160.7 mg - CB15 cholesteric liquid crystal, BDH Chemicals  
160.7 mg - CE2 cholesteric liquid crystal, BDH Chemicals  
488.8 mg - E31 nematic liquid crystal, BDH Chemicals  
8.0 mg - BAB (4,4'-bisacryloylbiphenyl), lab synthesized monomer  
5 3.0 mg - BME (benzoinmethyl ether), Polyscience Co., photo-initiator  
2.2 mg - R4, dichroic dye

The material was irradiated with U.V. light for thirty minutes to polymerize the monomer and cause phase separation of the polymer into  
10 polymer domains in the cell. In the reflecting state the material reflected green color. In the scattering state the material appears black when a black absorbing layer is used on the back substrate.

#### Example 23

- 15 A multistable color reflecting display cell was made with the following materials:

- 15.8% CE2 cholesteric liquid crystal, BDH Chemicals.  
14.8% CB15 cholesteric liquid crystal, BDH Chemicals.  
68.2% ZLI-4389 nematic liquid crystal, EM Industries, Inc.  
20 1.2% DSM DesSolite 950-044 uv material, DSM Desotech Inc.

A cell was prepared as in the previous examples. The DesSolite is a mixture of monomer, oligomer and photo-initiator. In the reflecting state the cell reflects green color.

25

#### Example 24

- A bistable light shutter was prepared where the pitch length of the liquid crystal was adjusted to reflect light in the ultra violet range. A mixture of 6.3% CE2 cholesteric liquid crystal, 6.2% CB15 cholesteric liquid crystal, 6.3% R-1011 chiral agent, 80% ZLI-4469-00 nematic liquid crystal mixture, 1% BAB  
30 bisacrylate monomer and 0.1% BME photo-initiator was introduced between glass plates coated with ITO to serve as transparent electrodes. The glass plates were coated with polyimide and buffed to produce homogeneous alignment of the liquid crystal. The sample was irradiated by U.V. light to polymerize the

monomer and form phase separated polymer domains in the cell. The cell exhibited a stable optically clear state when switched to the planar texture and a stable scattering state when switched to the focal conic texture.

5 Many modifications and variations of the invention will be apparent to those skilled in the art in light of the foregoing detailed disclosure. Therefore, within the scope of the appended claims, the invention can be practiced otherwise than as specifically shown and described.

CLAIMS

## WHAT IS CLAIMED:

1. A light modulating cell comprising liquid crystalline light modulating material of liquid crystal and polymer, the liquid crystal being a chiral nematic liquid crystal having positive dielectric anisotropy and including chiral material in an amount effective to form focal conic and twisted planar textures,  
5 the polymer being distributed in phase separated domains in the cell in an amount that stabilizes the focal conic and twisted planar textures in the absence of a field and permits the liquid crystal to change textures upon the application of a field.
- 10 2. The cell as claimed in Claim 1 wherein the chiral nematic liquid crystal has a pitch length that reflects light outside the visible spectrum.
3. The cell as claimed in Claim 1 wherein the chiral nematic liquid crystal has a pitch length that reflects light in the infra-red spectrum.
- 15 4. The cell as claimed in Claim 1 wherein the pitch length of the chiral nematic liquid crystal is in a range of from about 1.0 to about 4.0 microns.
5. The cell as claimed in Claim 1 wherein the pitch length of the  
20 chiral nematic liquid crystal is in a range of from about 0.5 to about 1.0 microns.
6. The cell as claimed in Claim 1, 2, 3 or 4 wherein the chiral nematic liquid crystal contains from about 1 to about 16% by weight chiral material based on the combined weight of nematic liquid crystal and chiral material.
- 25 7. The cell as claimed in Claim 1 wherein the chiral nematic liquid crystal has a pitch length that reflects light in the visible spectrum.
8. The cell as claimed in Claim 7 wherein the pitch length of the  
30 chiral nematic liquid crystal is in a range of from about 0.25 to about 0.44 microns.

- 35 9. The cell as claimed in Claim 7 wherein the chiral nematic liquid crystal contains from about 27 to about 66% chiral material based on the combined weight of nematic liquid crystal and chiral material.
10. The cell as claimed in Claim 1, 2 or 7, including cell wall structure treated to align the liquid crystal molecules.
- 40 11. The cell as claimed in Claim 1, wherein the polymer is present in an amount of from about 1.5 to about 40% based on the total weight of polymer and liquid crystal in the cell.
- 45 12. The cell as claimed in Claim 1, 2 or 3 wherein the polymer stabilized liquid crystal is characterized by homeotropic alignment in a field-ON condition, and the surrounding regions of liquid crystal are characterized by a light scattering focal conic texture in the field-OFF condition and an optically clear homeotropic alignment in a field-ON condition.
- 50 13. The cell as claimed in Claim 1, 2 or 3 wherein the polymer stabilized liquid crystal is characterized by a twisted planar texture in a field-OFF condition, and the surrounding regions of liquid crystal are characterized by an optically clear twisted planar texture in a field-OFF condition and by a light scattering focal conic texture in a field-ON condition.
- 55 14. The cell as claimed in Claims 1 or 7 wherein the polymer stabilized liquid crystal exhibits a stable light reflecting twisted planar structure in a field-OFF condition following removal of a high field-ON condition, and a stable light scattering focal conic texture in a field-OFF condition following removal of a low field-ON condition.
- 60 15. In a method of addressing a light modulating cell containing a polymer stabilized chiral nematic liquid crystal material capable of being switched between a stable color reflecting state that reflects a maximum reference intensity and a stable light scattering state exhibiting a minimum



65 reference intensity of reflection by application of a voltage pulse, the  
improvement comprising the steps of applying voltage pulses of varying  
magnitude sufficient to achieve a continuum of stable states having color  
reflectivity of an intensity between said maximum and minimum reference  
intensities.

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16. The improvement according to claim 15 comprising applying  
square A.C. voltage pulses.

17. The improvement according to claim 15 comprising applying said  
75 pulses at a magnitude below that which will switch said material from said  
reflecting state to said scattering state.

18. A method of selectively adjusting the intensity of reflection of  
colored light from a light modulating material of chiral nematic liquid crystal and  
80 polymer, between a maximum and a minimum intensity comprising subjecting  
said material to an electric field pulse of sufficient duration and voltage to cause  
a first proportion of said chiral nematic material to exhibit a first optical state  
and a second proportion of said chiral nematic material to exhibit a second  
optical state, whereby said material will continuously reflect a selected intensity  
85 between said maximum and minimum that is proportional to the amount of said  
material in said first optical state.

19. The method according to claim 18 wherein said chiral nematic  
material in said first optical state exhibits a planar texture and said chiral  
90 nematic material in said second optical state exhibits a focal conic texture.

20. A light modulating device comprising liquid crystalline light  
modulating material of phase-separated domains of polymer and chiral nematic  
liquid crystal having positive dielectric anisotropy, wherein a first proportion of  
95 said material is in a first optical state and second proportion of said material is  
in a second optical state, and means for establishing an electrical field through  
said material, said means adapted to provide a pulse of sufficient voltage and

duration to change the proportion of said material in said first optical state, whereby the intensity of light reflected may be selectively adjusted.

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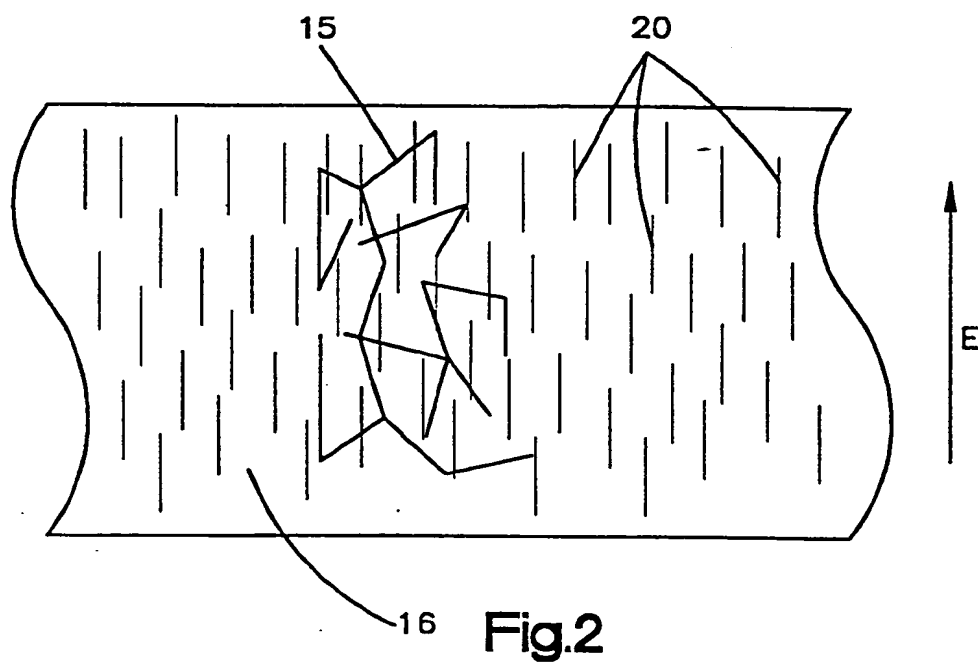
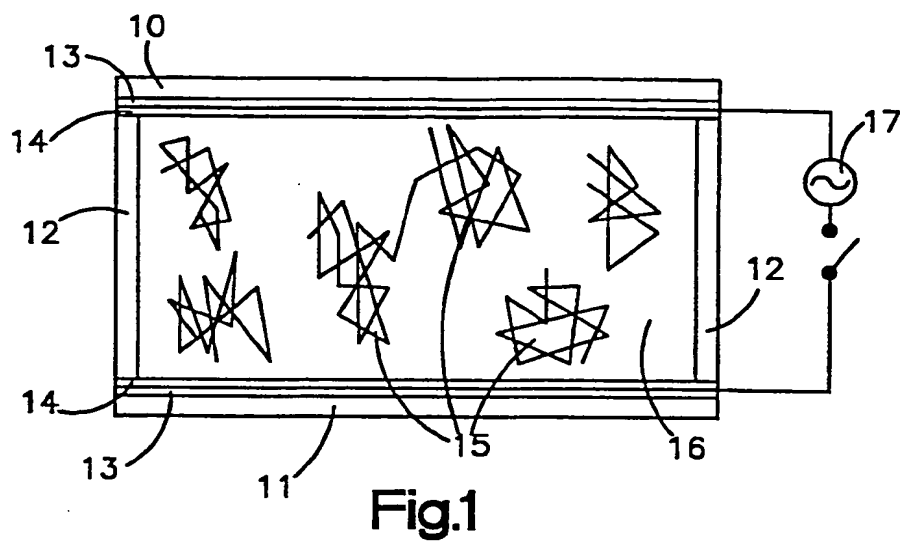
21. The device according to claim 20 wherein the material in said first optical state exhibits a planar texture and the material in said second optical state exhibits a focal conic texture.

105

22. The device according to claim 20 including cell wall structure treated to align the liquid crystal.

23. The device according to claim 20, wherein said means for establishing a field through said material is adapted to provide an AC pulse.

110



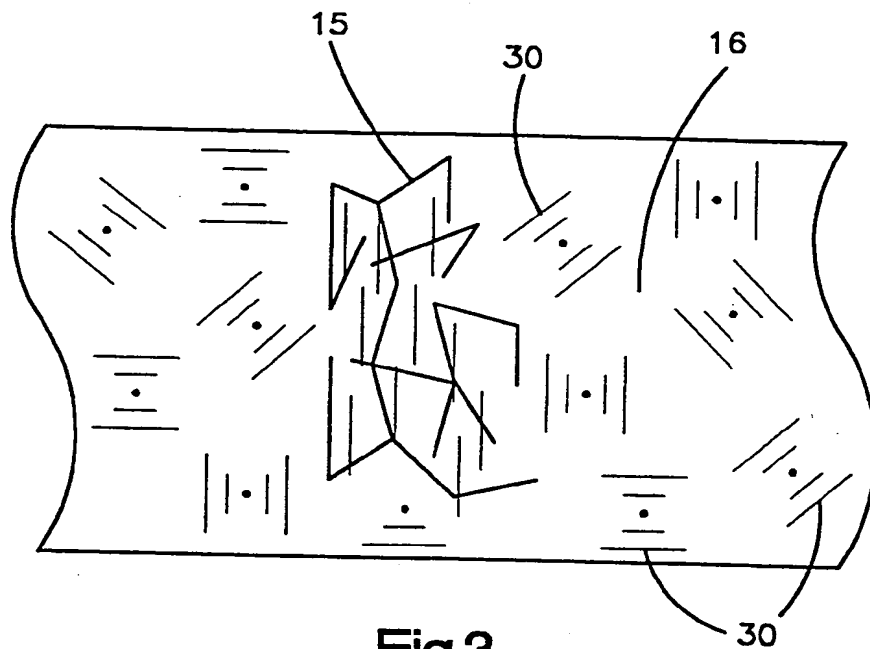


Fig.3

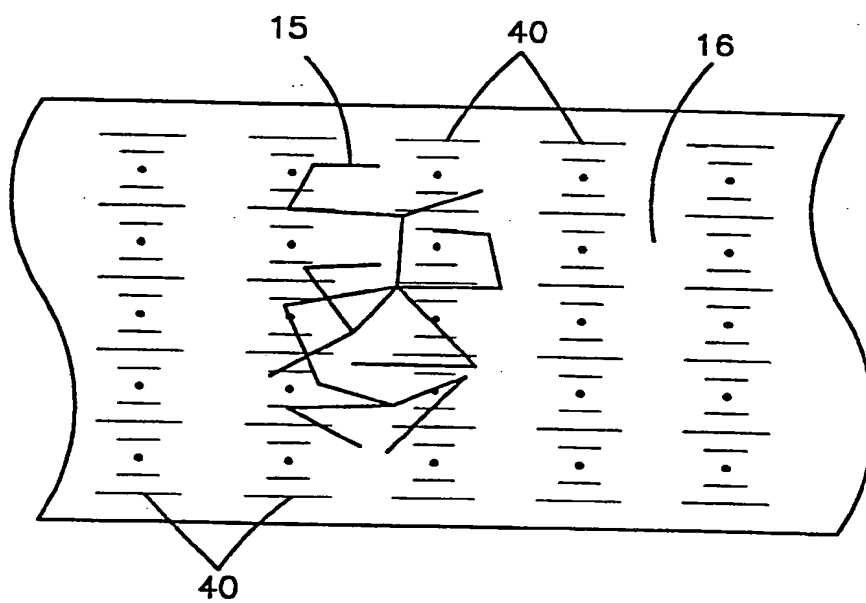


Fig.4

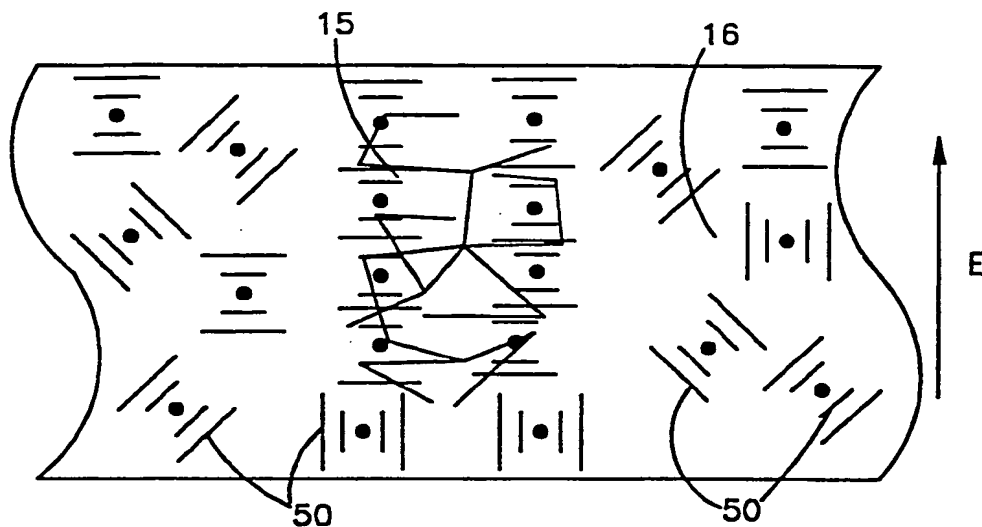


Fig.5

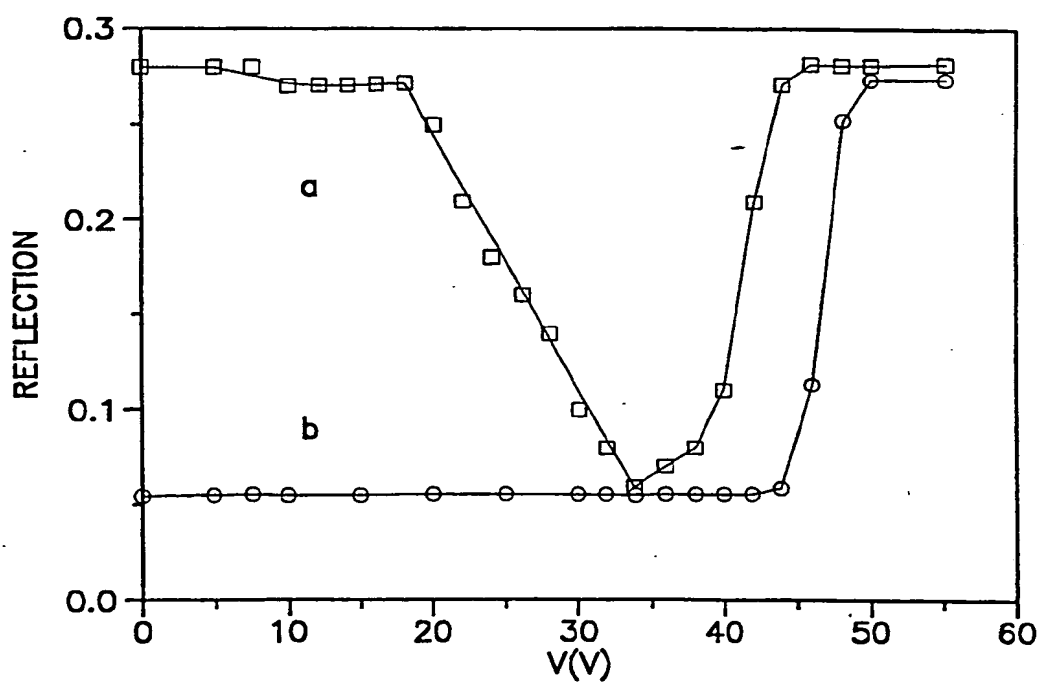


Fig.6

## INTERNATIONAL SEARCH REPORT

international application No.  
PCT/US92/09367**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :C09K 19/52; G02F 1/13

US CL :252/299.01; 359/51, 52, 91, 101

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/299.01; 359/51, 52, 91, 101

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS - Liquid crystal? and (chiral nematic or cholesteric) and polymer and (focal conic) and (Twisted planar).

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<u>Y,P</u> X,P	US, A, 5,138,472 (JONES ET AL.) 11 AUGUST 1992 See column 4, line 39 - column 5, line 35	<u>2-23</u> 1
Y	US, A 4,994,204 (DOANE ET AL.) 19 FEBRUARY 1991 See column 5	12-14
Y	US, A, 4,890,902 (DOANE ET AL.) 02 JANUARY 1990 See claims 1-3	10, 22
Y, E	US, A, 5,172,256 (SETHOFER ET AL.) 15 DECEMBER 1992 See column 13, line 39 - column 14, line 12	1-23
Y	US, A, 3,656,909 (DIXON ET AL.) 18 APRIL 1972 Whole document.	1-23

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

18 FEBRUARY 1993

Date of mailing of the international search report

16 MAR 1993

Name and mailing address of the ISA/US  
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/09367

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,600,060 (KETTERING) 17 AUGUST 1971 Whole document.	1-23

Form PCT/ISA/210 (continuation of second sheet)(July 1992)\*

